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Effect of Bentonite and Zeolite on Durability of Cement Suspension under Sulfate Attack

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The sulfate resistance of cement-bentonite suspension with additive lime is compared with that of a suspension where bentonite was totally replaced by pozzolanic zeolite. Cement-bentonite suspensions are frequently used for the construction of underground sealing walls. The disadvantage of these suspensions is due to a relatively low resistance against the aggressive media. With the purpose of obtaining sulfate-resistant suspension, a cement-zeolite suspension with the viscosity (Marsh cone) of 35 sec, the maximum settlement of 3 percent volume/24 hr and minimal compressive strength (28 days curing in water) of 2.0 MPa (290 psi) was prepared.

In the 10 percent sodium sulfate solution, a total destruction of the cement-bentonite suspension test specimens took place within 30 days. No degradation was found in the cement-zeolite suspension attacked by the sulfate solution for 365 days. Moreover, the cement-zeolite suspension showed an increase in compressive strength.

It is supposed that the reason for this lies in the high reactivity of zeolite towards lime and intensive consumption of calcium hydroxide by pozzolanic reaction of zeolite. The SO_3 bonding and resulting calcium sulfate dihydrate development is markedly decreased in the cement-zeolite suspension compared with cement-bentonite suspension.

Keywords: bentonite; corrosion; sulfate attack.

INTRODUCTION

Sulfate attack has been an important subject of research, especially since various cements were found to insure the resistance of concrete against sulfate environment, particularly when cements with a low content of C_3A were used.[1-4]

According to many authors, two types of sulfate corrosion may be distinguished: the corrosion caused by the formation of calcium sulfate dihydrate ($C\bar{S}H_2$), and the corrosion caused by the formation of ettringite ($C_6A\bar{S}_3H_{32}$). The $C\bar{S}H_2$ corrosion of the cement composites is asserted in the aggressive media with a minimum concentration of 1000 mg $SO_4^{2-}.l^{-1}$.[1,5-7]

The next important factors increasing the resistance of concrete against sulfate corrosion are the replacement of portland cement by fly ash, silica fume, blast furnace slag, and trass;[8-11] the fineness of cement and pozzolan;[12] the amount of pozzolanic materials;[13,14] and concentration of the reactant concerned in the pore solution.[15]

Since pozzolanic reaction consumes a part of calcium hydroxide (CH) produced by the hydration of cement, the quantity of $C\bar{S}H_2$ formed in Eq. (1) will be smaller in blended cements than in plain ones.

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \leftrightarrow CaSO_4.2H_2O + NaOH \qquad (1)$$

The molecular volume of CH is approximately 33.2 ccm, whereas that of $C\bar{S}H_2$ is almost 74.3 ccm. This enlargement in volume between both compounds is the reason for expansion and degradation of the test specimens.

The conversion of CH to $C\bar{S}H_2$ in blended cements is connected with the formation of CSH gel that successfully fills and segments larger pores into smaller, discontinuous ones through pore-size and grain-size refinement. This involves the transformation of bulky CH crystals into a tremendously large number of amorphous CSH gels, thereby significantly diminishing the permeability and diffusion of SO_4^{2-} ions into the interior of the specimen.[9]

The partial substitution of cement by zeolitic addition allows for preparation of blended cements with technical performance better than those of the typical pozzolanic cements made from silica fume and blast furnace slag. The increase in compressive strength may be interpreted on the basis of a higher reactivity of zeolitic rocks towards lime than those with vitreous counterparts.[16,17]

RESEARCH SIGNIFICANCE

Cement-bentonite suspensions (CBS) are used mainly in underground sealing walls with a compressive strength between 0.2 and 0.8 MPa (29 to 116 psi) and a coefficient of permeability between 1.10^{-8} to 1.10^{-11} m.s^{-1}.[18,19] The disadvantage of CBS is due to a relatively low resistance against the attack of underground aggressive media.[20-22] To remove this negative feature of CBS, bentonite was partially replaced by zeolite in composition of suspension. It was proven that the

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compressive strength and the resistance of such a suspension in underground sealing walls contacted with an aggressive water (2000 mg of sulfates.l^{-1}, pH = 4.5) were higher than those made only with bentonite addition.[23] The increase in resistance of the suspension by utilization of zeolite and lime is shown in this paper.

EXPERIMENTAL WORK

Materials

Class 40 portland cement and hydraulic lime were used in all mixes. Bentonite with at least 70 percent content of montmorillonite, zeolite with at least 75 percent of the clinoptilolite content and remaining portion of alkali feldspars and quartz, and hydraulic lime with at least 90 percent of CaO were used. The properties of the cement are given in Table 1, and those of bentonite and zeolite in Table 2. Mix proportions of the CBS and CZS are listed in Table 3 and 4.

Test procedures

Cement suspensions were prepared under laboratory conditions [20 C, 60 percent relative humidity (RH) in air] and adjusted on the same value of viscosity estimated by the Marsh cone = 35 sec and maximum settlement = 3 percent volume within 24 hr. The Marsh cone, with a volume of 1500 cm^3, is used for the estimation of fluidity of fresh suspensions. The fluidity is determined by the rate of flow in sec for the suspension to filter through the cone and fill the bottom vessel with a volume of 946 cm^3. The fluidity is expressed as viscosity of suspension according to the Marsh cone. The viscosity of fresh suspension is compared to that of water. Viscosity of water at a temperature of 20 C is 28 sec. Sedimentation of fresh suspension is estimated in the volumetric cylinder with a volume of 1000 cm^3. The separation of suspension from water is given by a number of graduations of water divided from the suspension after 24 hr of settling. Sedimentation is expressed in percent volume. Due to a higher water adsorption capacity of bentonite than zeolite, a lower bentonite content was needed for the same viscosity and maximum settlement of both suspensions.

To maintain the same consistency, a lime addition in the amount of one-third of the bentonite portion in CBS and one-fourth of the zeolite portion in CZS was required. Fresh mixes were placed into 120 x 20 x 20-mm molds and cured at 95 percent RH at 20 C for 7 days and then in water for 21 days. After this basic curing, the test specimens were kept for 365 days in a water and 10 percent sodium sulfate ($N\bar{S}$) solution (an average 67,000 mg $SO_4^{2-}.l^{-1}$) at the ambient temperature. The $N\bar{S}$ solution was regularly checked for the concentration of sulfate ions. The test specimens were tested on compressive strength, dynamic modulus of elasticity (DME), and weight changes. The surface damage of the specimens was controlled by visual observations. The content of SO_3 bound in the cement suspensions was estimated by chemical analysis. The phase composition was recognized in a semi-quantitative manner using X-ray diffraction analysis on the apparatus with goniometer PW 1050 under these conditions: radiation CuK_α; voltage tension 40 kV; intensity 20 mA; and Ni- filter.

RESULTS AND DISCUSSION

The results show an extreme weight increase in the CBS test specimens attacked for 30 days by the sulfate solution (Fig. 1). On the contrary, weight changes in CZS remain negligible for 365 days. The SO_3 bonding in CZS is markedly slowed down compared with CBS (Fig. 2). Total destruction of CBS characterized by disintegration of the specimen takes

Table 1—Standard strength, composition, and properties of cement

	Cement strength, MPa									
Days	Flexural				Compressive					
3	4.4				23.5					
28	7.9				41.7					
Component content, weight percent	Ins. res.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Ign. loss
	1.63	20.64	5.88	3.13	61.49	1.34	2.30	1.82	0.53	1.04
Beginning of setting	3 hr, 15 min									
Setting time	4 hr, 20 min									
Density, kg.m^{-3}	Specific surface area, $m^2.kg^{-1}$						Content of (Bogue), percent			
3140	336.2						C_3S	C_2S	C_3A	C_4AF
							49.45	21.88	10.28	9.53

Table 2—Composition and properties of bentonite and zeolite

Component content, weight percent	Ign. loss	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	SO_3	Specific surface area, $m^2.kg^{-1}$
Na-bentonite	15.66	43.09	4.53	2.58	17.79	15.32	0.55	961
Zeolite	12.44	66.72	5.25	0	13.70	1.69	0.19	1150

Table 3—Composition of cement-bentonite suspension

Constituent	Portion
Portland cement	1000 g
Bentonite	187.5 g
Hydraulic lime	62.5 g
Water	1250 ml
Ratio of portland cement to bentonite and lime	80: 15: 5

Table 4—Composition of cement-zeolite suspension

Constituent	Portion
Portland cement	1000 g
Zeolite	250 g
Hydraulic lime	62.5 g
Water	1250 ml
Ratio of portland cement to zeolite and lime	76: 19: 5

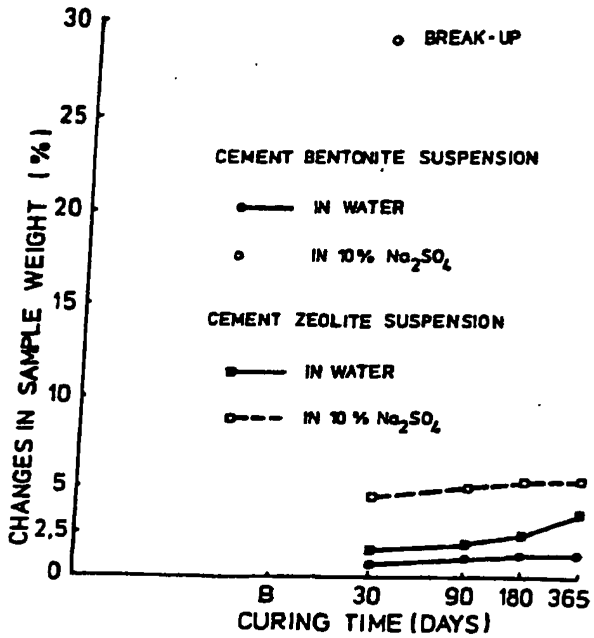

Fig. 1—Weight increase of tested specimens.

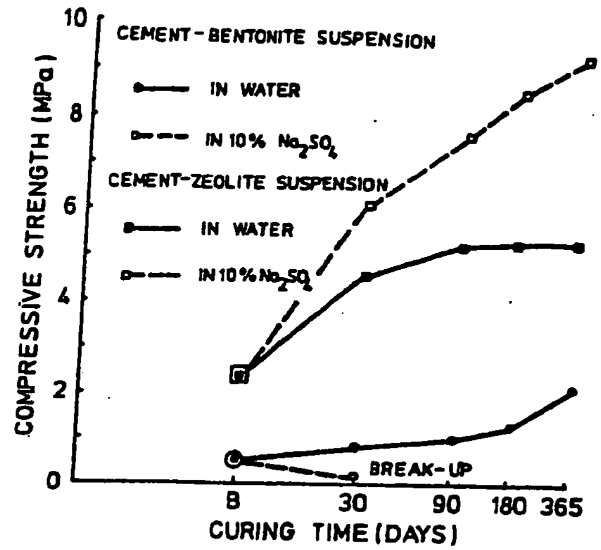

Fig. 3—Changes in compressive strength of tested specimens.

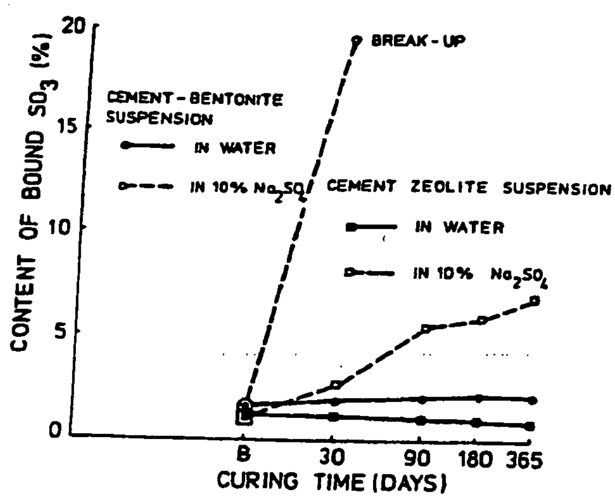

Fig. 2—Values of So_3 content bound in tested suspensions.

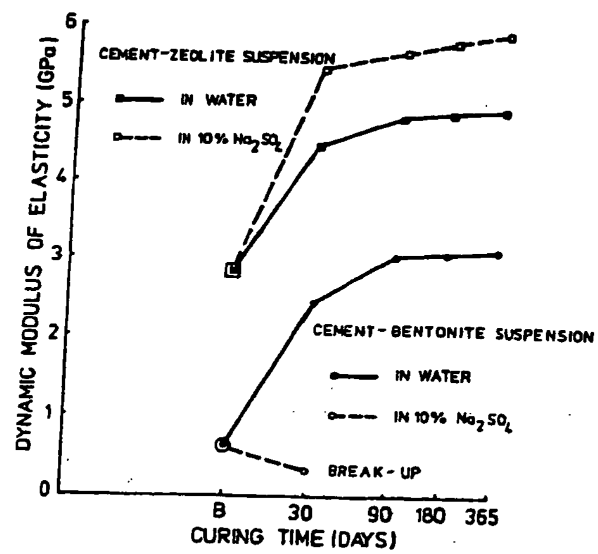

Fig. 4—Changes in dynamic modulus of elasticity of tested specimens.

place at the 20 percent content of bound SO_3 in CBS cured in the sulfate solution. In CZS, the increase in SO_3 content is low. It is evident that the reduced weight increase and SO_3 bonding in CZS is a result of the zeolite addition to cement. The increase in compressive strength and DME is observed in CZS, whereas a total destruction of CBS was attained at the 30-day exposure in the sulfate solution (Fig. 3 and 4).

Fig. 5 demonstrates that mainly CH is the reaction product developed in the phase composition of both suspensions after basic curing. The CH content is less in the CZS than in

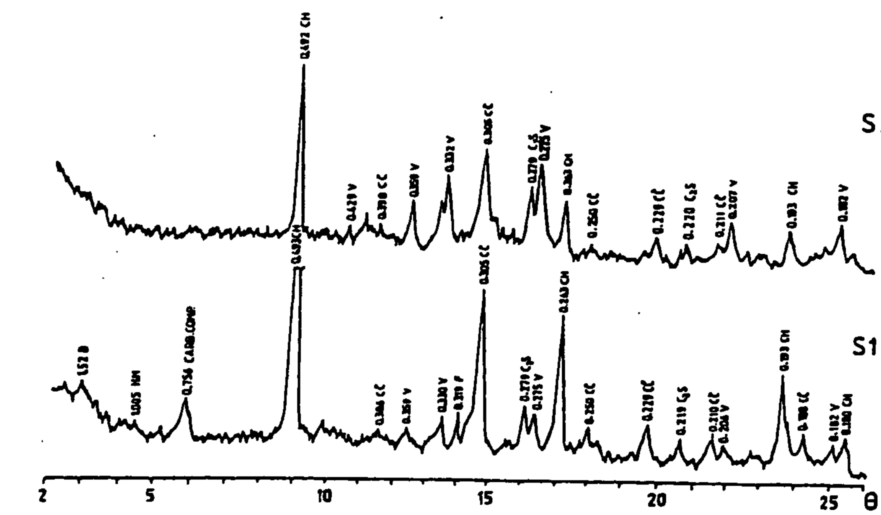

Fig. 5—X-ray diffraction patterns of CBS (S1) and CZS (S2) after 28 days of curing in water.

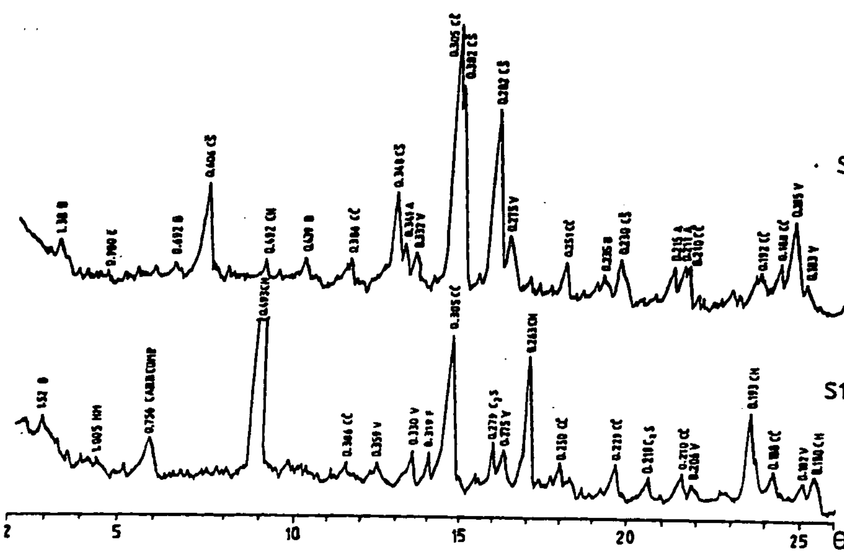

Fig. 6—Results of X-ray diffraction analysis of CBS after 28 days of curing in water (S1) and then 30 days in 10 percent sodium sulfate solution (S7).

the CBS. The remaining CH is converted to carbonation products. A high $C\bar{S}H_2$ content developed in the CBS subjected to the $N\bar{S}$ solution is shown in Fig. 6. The $C\bar{S}H_2$ formation is evidently restrained in the CZS (Fig. 7). The presence of calcium silicate hydrates and calcium silico-aluminate hydrates as products (CSH and CSAH) is indicated in Pattern S22 by the diffraction of low intensity at 11.9 Å (1.19 nm) belonging to the tobermorite-like phase.

The comparison of the beginning materials shows that the SiO_2 content is different in both materials, as shown in Table 2. The content of SiO_2 has about 23 percent more weight of zeolite than bentonite. It is evident (Table 3 and 4) that the portion of bentonite is 15 percent weight and zeolite is 19 percent weight in the suspension when calculated on the content of dry constituents. The SiO_2 content from bentonite is 80.8 g and zeolite is 166.8 g. This SiO_2 increase due to the substitution of bentonite by zeolite undoubtedly enhances the reactivity of zeolite towards the CaO component of portland cement and additive lime.

Differences in the composition and structure of bentonite and zeolite are the main reasons influencing the resistance of suspensions against the $N\bar{S}$ attack. Zeolite represents a volcanic sedimentary authigenic rock in which clinoptilolite by the conversion of SiO_2-rich vitreous ash to the mass of zeolitic tuff in the alkaline environment was converted. Bentonite is a clay with a prevailing content of the smectite group of minerals (mainly montmorillonite). Conversion of pyroclastics and effusives in the lake and sea environment was the cause of the rise in bentonite. An alumino-silicate skeleton structure of zeolite enables its ion exchange and

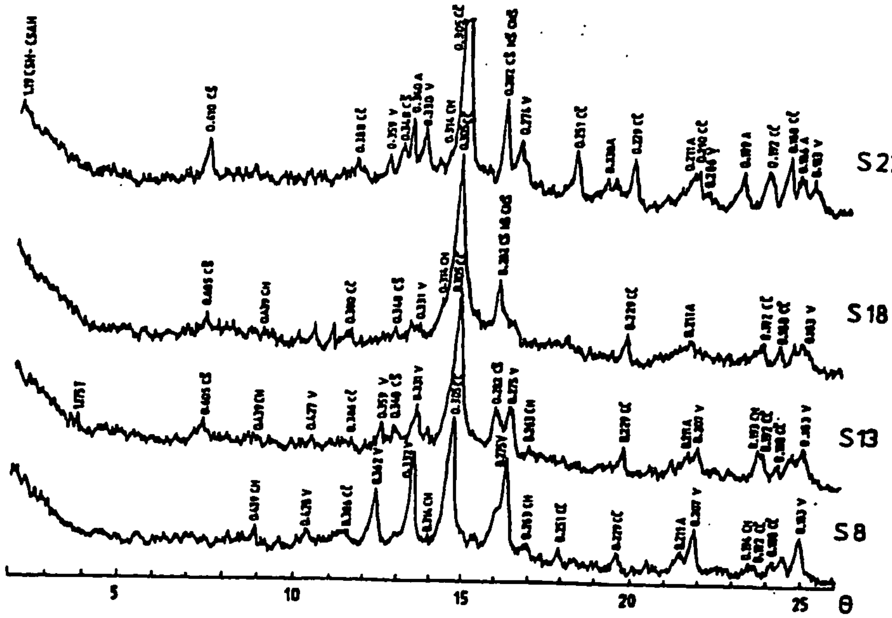

Fig. 7—Results of X-ray diffraction analysis of CZS after 30 days (S8); 90 days (S13); 180 days (S18); and 360 days (S22) of curing in 10 percent sodium sulfate solution when the specimens were first kept under water for 28 days (see sample S2).

adsorption of molecules of different sizes on the zeolite grains without the impairment of their surfaces. This predetermines zeolites for sorbents, molecular sieves, and catalysts.[24-26] Such zeolite property is confirmed by values of ion-exchange capacity with maxima to K^+1.88 mmol.g^{-1}, Ca^{2+}1.82 mmol.g^{-1}, Cs^+0.61 mmol.g^{-1}, Mg^{2+}0.24 mmol.g^{-1}, Co^{2+}0.14 mmol.g^{-1}, Ba^{2+}0.13 mmol.g^{-1}, and Na^+0.13 mmol.g^{-1}.

A porous zeolite structure with an effective average pore diameter of 0.35 nm enables a surface near alternation of exchangable cations between zeolite and its surroundings. The reactional ability of zeolite to bind with lime is higher than that of bentonite, which is confirmed by higher compressive strength and DME in the CZS than those in the CBS cured in water and an $N\bar{S}$ solution.

The probable cause of this may be explained by the study of phases detected under the reaction of zeolite (clinoptilolite) and quartz with CaO[27] under saturated steam pressure. In the first case, the major phase was found at 11 Å (1.1 nm), an Al-rich tobermorite by treating the clinoptilolite-lime mix. By contrast, unreacted quartz $Ca(OH)_2$, Ca-Si gel, and partial tobermorite were found in the quartz-lime mix.

A gradual chemical bonding of CH by zeolite causes the pronounced restriction in the $C\bar{S}H_2$ development in the $N\bar{S}$ solution. The reduction in the $C\bar{S}H_2$ rise is closely connected to the pozzolanic reaction of CH with zeolite when the CSH and CSAH hydration products are prevailingly formed in the CZS, compared with that of the CBS, where CH mainly occurs. The SiO_2 in the zeolite consumes all of the lime in the CZS to develop less permeable and denser gel-like hydration products instead of the bulky CH formed prevailingly in the CBS. This is confirmed by the higher compressive strength and DME, as well as the lower SO_3 content, weight increase, and surface damage of the CZS specimens when compared to the CBS specimens cured in the $N\bar{S}$ solution.

CONCLUSIONS

1. The replacement of bentonite by zeolite in cement suspension with additive lime extremely increases its resistance against the 10 percent sodium sulfate solution.

2. In a cement-zeolite suspension, the intensive binding of CaO by zeolite forms the reaction products rich in the calcium silicate and calcium silico-aluminate hydrates when compared to the $Ca(OH)_2$ content with consequent pronounced reduction in $CaSO_4.2H_20$ development.

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CONVERSION FACTORS

1 MPa	=	145 psi
1 kg.m^{-3}	=	1.685 lb/yd^{-3}
1 GPa	=	145 ksi
1 m^2.kg^{-1}	=	0.543 yd^2.lb^{-1}

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